

Precipitrimetry II

No indicator methods

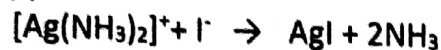
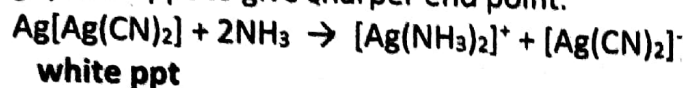
- 1- Disappearance of ppt.
(det. of Ag^+ with CN^-)
- 2- Appearance of ppt.
(det. of CN^- with Ag^+)
(Liebeg's method)
(Dengie's method)

Indicator methods

- 1- Colored ppt.
(Mohr's method)
- 2- Colored complex.
(Volhard method)
- 3- Adsorption Ind.
(Fajan's method)
- 4- External Ind.

	Disappearance of ppt.	appearance of ppt. (Liebeg's)
sample	Ag^+	CN^-
Standard	CN^-	Ag^+
e.p	disappearance of ppt.	appearance of ppt.
	$\text{AgNO}_3 + \text{KCN} \rightarrow \text{AgCN} \xrightarrow{\text{CN}^-} \text{K}[\text{Ag}(\text{CN})_2]$ (white ppt) (sol. complex) Argentocyanide	$\text{AgNO}_3 + \text{KCN} \rightarrow \text{AgCN} \xrightarrow{\text{CN}^-} \text{K}[\text{Ag}(\text{CN})_2]$ (white ppt) (sol. complex)

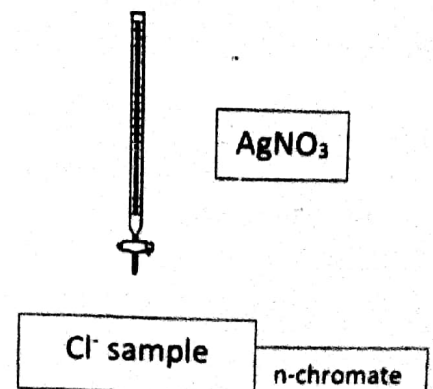
Dengie's method (modification of Liebeg's) Addition of iodide in ammoniacal medium. why?
To form more insoluble AgI yellow ppt to give sharper end point.



Only Ag_2S can interfere in Liebeg's method while halides and thiocyanate not interfere
 Ag^+ released from the dissociation of $[\text{Ag}(\text{CN})_2]^-$ is not sufficient to exceed the solubility product of halides but sufficient to exceed that of Ag_2S

Indicator Methods

1- Mohr's method (coloured product)	
sample	Cl^- , Br^-
Standard	Ag^+ (argentometry)
Indicator	neutral chromate (yellow)
E.P	appearance of brick red ppt (Ag_2CrO_4)
Medium	Neutral, slightly alkaline pH (7-9)



Problem	Ksp of $\text{Ag}_2\text{CrO}_4 < \text{AgCl}/\text{AgBr}$ So should ppt. first	
الحل (solution)	Retard pptn. of Ag_2CrO_4 by preparing as dilute solution (0.002- 0.005M)	
Blank	Why?	Amount of AgNO_3 consumed to give detectable quantity of ppt to human eye.
	How?	Suspension of CaCO_3 or Talc # AgNO_3 in presence of n-chromate
pH (7-9)	If >9	Silver will ppt. as oxide $\text{Ag}^+ + 2\text{OH}^- \rightarrow \text{AgOH} \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O}$
	If <7	Formation of $\text{Cr}_2\text{O}_7^{2-}$ which is more soluble than CrO_4^{2-} (over consumption) $\text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$
Suitable for	Easily hydrolysable salt as chloro or bromo derivative as acetyl chloride $\text{CH}_3\text{COCl} + 2\text{NaOH} \rightarrow \text{NaCl} + \text{CH}_3\text{COONa} + \text{H}_2\text{O}$ ↪ Titrated against AgNO_3	
Not suitable for	# iodide , thiocyanate: -Adsorb chromate ion. - yellow ppt. of AgI render the e.p difficult	
	# Ammonium salts: - in alkaline medium pH = 9 NH_4OH formed which dissolves the ppt.	
	# Halides in prescence of CO_3^{2-}, PO_4^{3-}, oxalate: - as (molar solubility→ksp) less than or equal that of chromate.	

2- Volhard method (coloured complex)		
	Indirect volhard	Direct volhard
sample	Halides, CN^- , SCN^- , arsenate, Phosphate, oxalate	Ag^+ , Hg^{2+}
Standard	XSS std AgNO_3 (titrated with std. SCN^-)	SCN^-
Indicator	ferric alum	
e.p	Appearance of blood red colour $\text{Fe}^{3+} + 2\text{SCN}^- \rightarrow [\text{Fe}(\text{SCN})_2]^+$	
Medium	acidic	

Indicator: conc. = 0.2 M and not critical. Above it the yellow colour will interfere

Medium: Must be acidic to prevent pptn. of $\text{Fe}(\text{OH})_3$.

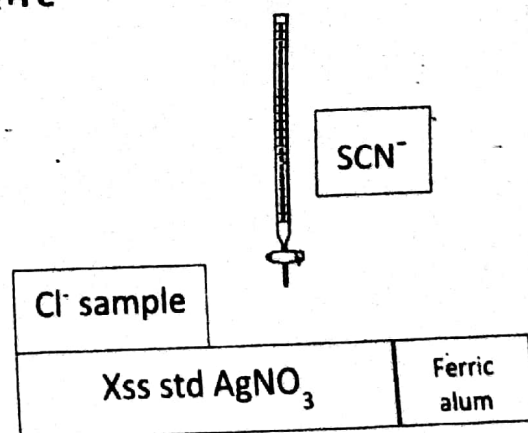
Iodide: Ferric alum added after pptn. of I^- . **Why?** $\text{I}^- + \text{Fe}^{3+} \rightarrow \text{I}_2 + \text{Fe}^{2+}$

Chloride: Ksp $\text{AgSCN} < \text{AgCl}$



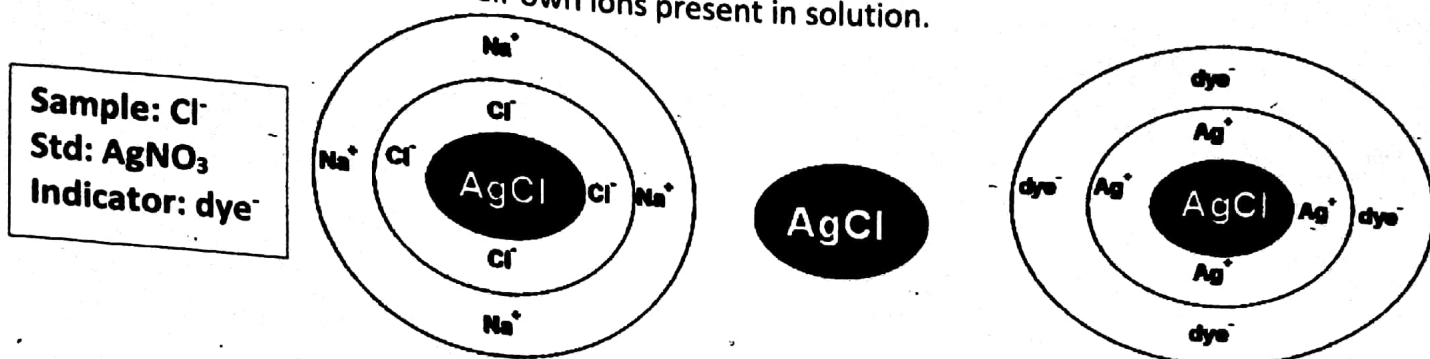
To overcome this:

- 1- filtration of the white ppt. of AgCl .
- 2- add nitrobenzene to coat the ppt.



3- Fajan's method (adsorption indicators)

Adsorption ind.: Acidic or basic dyes which change their colour on adsorption on the ppt. at E.P
Theory: Colloidal ppt adsorb their own ions present in solution.



For successful use of adsorption indicator:
Ppt must be:

- 1- Colloidal $\rightarrow \uparrow$ surface area $\rightarrow \uparrow$ adsorption of indicator.
- 2- The ppt. must strongly adsorb its own ion.

Indicator:

- 3- The indicator dye must be of **opposite charge with the precipitating titrant**
 titrant silver $\rightarrow$ fluorescein, eosin (anionic dye) acidic.
 titrant chloride $\rightarrow$ rhodamine 6G (cationic dye) basic.
- 4- The indicator ion should **not be adsorbed before** the particular compound has been completely precipitated (e.p).
- 5- The concentration the indicator **not ppt.** during the titration or even after e.p

pH:

- 6- The pH of the solution must **assure ionization of the indicator**
 Fluorescein (weak acidic) $\rightarrow$ neutral to slightly alkaline medium pH= 7-9
 Eosin (stronger) $\rightarrow$ pH=2
 dichlorofluorescein $\rightarrow$ pH=4

7- **Avoid** the presence of **polyvalent ions** owing to their **coagulating effect**.

8- **coagulation** of ppt. is **prevented** by various protective colloids **dextrin, starch**

Eosin cannot be used as indicator for chloride?

Eosin strongly adsorbed and would replace some of the chloride ion before the e.p in the primarily adsorbed layer giving an earlier e.p but Can be used with iodide and bromide.

Application of Fajan's method:

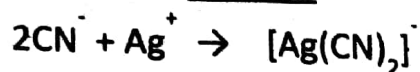
- 1- Fluorescein $\rightarrow$ for determination of Cl^- , Br^- , I^- , SCN^- .
- 2- Eosin $\rightarrow$ for determination of Br^- , I^-
- 3- Rose bengal $\rightarrow$ Determination of I^- in presence of Cl^- .
- 4- Rhodamine 6G $\rightarrow$ for determination of Ag^+ with Br^- .

Mix. of Cl^- or Br^- / CN^-

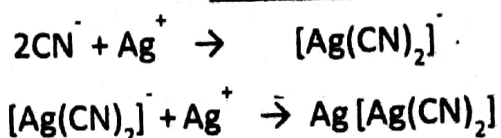
- 1- total by volhard's.
- 2- cyanide by Liebeg's

The volume of AgNO_3 taken by CN^- in volhard is double reading in liebeg's

Liebeg's



Volhard's



In case of Cl^-/CN^- mix. Filtration should be done **Why?**

4- External indicator:

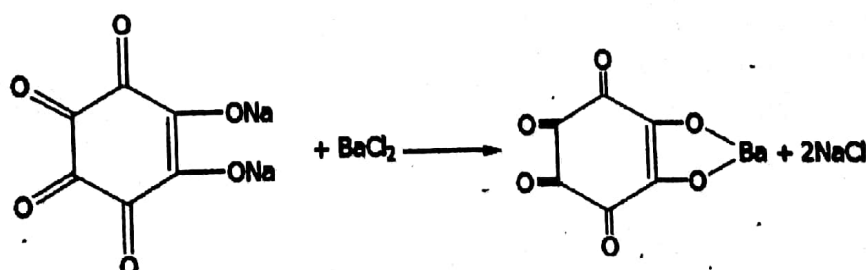
Used for: Zn^{2+} ions

Titrant: potassium ferrocyanide - $\text{K}_4\text{Fe}(\text{CN})_6$

Medium: neutral or acidic

Indicator: external indicator – Uranyl nitrate

End point: brown colour



Sod. Rhodizonate
colourless

Barium rhodizonate
Red ppt

sample	Barium	Sulphate
Type of determination	direct	back
titrant	Standard sodium sulphate	
Indicator	Sodium rhodizonate	
End point	Disappearance of red ppt	
	Barium directly titrated against std sodium sulphate	Sulphate + xss barium chloride, residual barium chloride is titrated against sodium sulphate
KSP of barium sulphate is < KSP of barium rhodizonate		